

Method for Producing Thermoplastic Polyurethane Elastomers
~~Process for preparing thermoplastic polyurethane elastomers~~

The present invention relates to a process for preparing thermoplastic polyurethane elastomers, the products resulting therefrom and their use.

Thermoplastic polyurethanes (TPU) are used very widely because they have good elastomer properties and can be readily processed. A very wide range of mechanical properties can be produced by suitable selection of the components. A review of TPUs, their properties and applications is given e.g. in Kunststoffe 68 (1978) 819, Kautschuk, Gummi, Kunststoffe 35 (1982) 569; G. Becker, D. Braun: Kunststoff-Handbuch, vol. 7 "Polyurethane" Munich, Vienna, Carl Hanser Verlag 1983. A review of methods of preparation is given in Plastikverarbeiter 40 (1989).

TPUs are generally built up from linear polyols, such as polyesterpolyols or polyetherpolyols, organic diisocyanates and short chain, generally difunctional, alcohols (chain lengtheners). They may be prepared batchwise or continuously.

The continuous extrusion process has been known for some time. In this process the starting materials are metered into a screw reactor, polycondensed there and then converted into a uniform granular form (US-A 3 642 964, DE-C 23 02 564, DE-C 25 49 371, DE-A 32 30 009, EP-A 31 142).

The extrusion process is comparatively simple, but has the disadvantage that the starting materials are mixed only in the reactor and under conditions under which polyaddition occurs extensively, which means that inhomogeneities and thus undesired, and uncontrollable, secondary reactions may occur.

EP-A 554 718 and EP-A 554 719 propose improving the extrusion process by feeding the starting materials into a nozzle and mixing them before entrance to the extruder. Since however the polyaddition reaction occurs only in the extruder, the

"Express Mail" mailing label number EK9833317360S

Date of Deposit June 6, 2000

I hereby certify that this paper or fee is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on the date indicated above and is addressed to the Assistant Commissioner of Patents and Trademarks, Washington, D.C. 20231

Donna J. Veatch

(Name of person mailing paper or fee)

Donna J. Veatch
Signature of person mailing paper or fee

products resulting from this process also have inhomogeneities which become obvious in particular in extrusion products such as films.

5 Methods of preparation are also known from the prior art in which the starting materials are first mixed in a mixing zone at temperatures at which no polyaddition takes place and then reacted with each other in a reaction zone which has the desired reaction temperature. The mixing and reaction zones are preferably designed as static mixers (DE-A 28 23 762, EP-A 747 409, EP-A 747 408).

10 It has now been found that TPUs with improved homogeneity and improved melting characteristics can be obtained when the difference between the temperatures of the starting materials used to prepare them is as small as possible prior to the mixing process.

15 Therefore the invention provides a process for the continuous preparation of thermoplastic polyurethane elastomers, in which

one or more organic isocyanates (A) and

20 a mixture (B) containing Zerewitinoff-active hydrogen atoms, comprising

B1) 1 to 85 equivalent-%, with respect to the isocyanate groups in (A), of one or more compounds with on average at least 1.8 Zerewitinoff-active hydrogen atoms and an average molecular weight \overline{M}_n of 450 to 10000,

25 B2) 15 to 99 equivalent-% (with respect to the isocyanate groups in (A)) of one or more chain lengthening agents with on average at least 1.8 Zerewitinoff-active hydrogen atoms and a molecular weight of 60 to 400, and

30

0955921.060600

0-20 wt.%, with reference to the total amount of TPU, of further auxiliary agents and additives (C)

are homogeneously premixed in a reactor within a period of at most 5 seconds, wherein the difference between the temperatures of components (A) and (B), before entering the reactor, is $< 20^{\circ}\text{C}$.

Organic isocyanates (A) which may be used include aliphatic, cycloaliphatic, araliphatic, aromatic and heterocyclic polyisocyanates or any mixtures of these polyisocyanates (see HOUBEN-WEYL "Methoden der organischen Chemie", vol. E20 "Makromolekulare Stoffe", Georg Thieme Verlag, Stuttgart, New York 1987, p. 1587-1593 or Justus Liebigs Annalen der Chemie, 562, pages 75 to 136).

The following may be mentioned individually, by way of example: aliphatic diisocyanates such as ethylene diisocyanate, 1,4-tetramethylene diisocyanate, 1,6-hexamethylene diisocyanate, 1,12-dodecane diisocyanate, cycloaliphatic diisocyanates such as isophorone diisocyanate, 1,4-cyclohexane diisocyanate, 1-methyl-2,4-cyclohexane diisocyanate and 1-methyl-2,6-cyclohexane diisocyanate as well as the corresponding mixtures of isomers, 4,4'-diisocyclohexylmethane diisocyanate, 2,4'-dicyclohexylmethane diisocyanate and 2,2'-dicyclohexylmethane diisocyanate as well as the corresponding mixtures of isomers, also aromatic diisocyanates such as 2,4-toluylene diisocyanate, mixtures of 2,4-toluylene diisocyanate and 2,6-toluylene diisocyanate, 4,4'-diphenylmethane diisocyanate, 2,4'-diphenylmethane diisocyanate and 2,2'-diphenylmethane diisocyanate, mixtures of 2,4'-diphenylmethane diisocyanate and 4,4'-diphenylmethane diisocyanate, urethane-modified liquid 4,4'-diphenylmethane diisocyanate or 2,4'-diphenylmethane diisocyanate, 4,4'-diisocyanatodiphenylethane-(1,2) and 1,5-naphthylene diisocyanate. 1,6-hexamethylene diisocyanate, 1,4-cyclohexane diisocyanate, isophorone diisocyanate, dicyclohexylmethane diisocyanate, diphenylmethane diisocyanate isomeric mixtures with a 4,4'-diphenylmethane diisocyanate content of more than 96 wt.% are preferably used, in particular 4,4'-

diphenylmethane diisocyanate and 1,5-naphthylene diisocyanate. The diisocyanates mentioned may be used separately or as mixtures with each other. They may also be used together with up to 15 mol.% (calculated from the total diisocyanate content) of a polyisocyanate, but the maximum amount of polyisocyanate added should be only
5 enough to produce a product which can still be thermoplastically processed. Examples of polyisocyanates are triphenylmethane-4,4',4"-triisocyanate and polyphenyl-polymethylene-polyisocyanates.

Zerewitinoff-active compounds (B1) which are used for the process according to the
10 invention are those with on average at least 1.8 to 3.0 Zerewitinoff-active hydrogen atoms and an average molecular weight \overline{M}_n of 450 to 10000.

Compounds included here are, in addition to compounds which possess amino groups, thiol groups or carboxyl groups, are compounds with in particular 2 to 3,
15 preferably 2 hydroxyl groups, in particular those with average molecular weights \overline{M}_n of 450 to 6000, especially those with an average molecular weight \overline{M}_n of 600 to 4500, e.g. polyesters, polyethers, polycarbonates and polyesteramides containing hydroxyl groups.

Suitable polyether diols may be prepared by reacting one or more alkylene oxides with 2 to 4 carbon atoms in the alkylene group with a starter molecule which contains two bonded, active, hydrogen atoms. The following may be mentioned as alkylene oxides: e.g. ethylene oxide, 1,2-propylene oxide, epichlorhydrin and 1,2-butylene oxide and 2,3-butylene oxide. Ethylene oxide, propylene oxide and
20 mixtures of 1,2-propylene oxide and ethylene oxide are preferably used. The alkylene oxides may be used separately, alternately one after the other or as mixtures. The following may be used, for example, as starter molecules: water, aminoalcohols such as N-alkyl-diethanolamines, for example N-methyl-diethanolamine and diols such as ethylene glycol, 1,3-propylene glycol, 1,4-
25 butanediol and 1,6-hexanediol. Optionally, mixtures of starter molecules may also be used. Suitable polyetherols are also hydroxyl group-containing polymerisation
30

0955921-060600

products of tetrahydrofuran. Trifunctional polyethers may also be used in proportions of 0 to 30 wt.% with respect to the bifunctional polyethers, but at most in amounts such that a product which is still thermoplastically processable is produced. The substantially linear polyether diols preferably have average molecular weights \overline{M}_n of 450 to 6000. They may be used either separately or in the form of mixtures with each other.

Suitable polyester diols may be prepared, for example, from dicarboxylic acids with 2 to 12 carbon atoms, preferably 4 to 6 carbon atoms and polyhydric alcohols. The following are suitable, for example, as dicarboxylic acids: aliphatic dicarboxylic acids such as succinic acid, glutaric acid, adipic acid, suberic acid, azaleic acid and sebacic acid, or aromatic dicarboxylic acids such as phthalic acid, isophthalic acid and terephthalic acid. The dicarboxylic acids may be used separately or as mixtures, e.g. in the form of a succinic, glutaric and adipic acid mixture. To prepare polyesterdiols, it may optionally be advantageous to use the corresponding dicarboxylic acid derivatives such as diesters of carboxylic acids with 1 to 4 carbon atoms in the alcohol group, carboxylic acid anhydrides or carboxylic acid chlorides, instead of the dicarboxylic acids. Examples of polyhydric alcohols are glycols with 2 to 10, preferably 2 to 6 carbon atoms e.g. ethylene glycol, diethylene glycol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,10-decanediol, 2,2-dimethyl-1,3-propanediol, 1,3-propanediol or dipropylene glycol. Depending on the properties required, the polyhydric alcohols may be used separately or as a mixture with each other. Also suitable are esters of carbonic acid with the diols mentioned, in particular those with 4 to 6 carbon atoms, such as 1,4-butanediol or 1,6-hexanediol, condensation products of ω -hydroxycarboxylic acids such as ω -hydroxycaproic acid or polymerisation products of lactones, e.g. optionally substituted ω -caprolactones. The following are preferably used as polyesterdiols, ethanediol-polyadipate, 1,4-butanediol-polyadipate, ethanediol-1,4-butanediol-polyadipate, 1,6-hexanediol-neopentylglycol-polyadipate, 1,6-hexanediol-1,4-butanediol-polyadipate and polycaprolactones. The polyesterdiols preferably have average molecular

weights \overline{M}_n of 450 to 6000 and may be used separately or in the form of mixtures with each other.

5 Zerewitinoff-active compounds (B2) are so-called chain lengthening agents and have on average 1.8 to 3.0 Zerewitinoff-active hydrogen atoms and have a molecular weight of 60 to 400. These are understood to include, in addition to compounds with amino groups, thiol groups or carboxyl groups, those compounds with two to three, preferably two hydroxyl groups.

10 Diols with 2 to 14 carbon atoms are preferably used as chain lengthening agents, such as e.g. ethanediol, 1,2-propanediol, 1,3-propanediol, 1,4-butanediol, 2,3-butanediol, 1,5-pentanediol, 1,6-hexanediol, diethylene glycol and dipropylene glycol. Also suitable however are diesters of terephthalic acid with glycols with 2 to 4 carbon atoms, e.g. terephthalic acid-bis-ethylene glycol or terephthalic acid-bis-
15 1,4-butanediol, hydroxalkylene ethers of hydroquinone, e.g. 1,4-di-(β -hydroxyethyl)-hydroquinone, ethoxylated bisphenols, e.g. 1,4-di-(β -hydroxyethyl)-bisphenol A, (cyclo)aliphatic diamines such as isophorone diamine, ethylene diamine, 1,2-propylene diamine, 1,3-propylene diamine, N-methyl-propylene-1,3-diamine, N,N'-dimethylethylene diamine and aromatic diamines such as 2,4-
20 toluylene diamine, 2,6-toluylene diamine, 3,5-diethyl-2,4-toluylene diamine or 3,5-diethyl-2,6-toluylene diamine or primary mono, di, tri or tetraalkyl substituted 4,4'-diaminodiphenyl methanes. Ethanediol, 1,4-butanediol, 1,6-hexanediol, 1,4-di-(β -hydroxyethyl)-hydroquinone or 1,4-di-(β -hydroxyethyl)-bisphenol A are particularly preferably used as chain lengtheners. Mixtures of the chain lengtheners mentioned
25 above may also be used. In addition small amounts of triols may also be used.

Compounds which are monofunctional with regard to isocyanates may be used in amounts of up to 2 wt.%, with respect to TPU, as so called chain terminators. Suitable compounds are e.g. monoamines such as butyl and dibutylamine, octylamine, stearylamine, N-methylstearylamine, pyrrolidine, piperidine or
30 cyclohexylamine, monoalcohols such as butanol, 2-ethylhexanol, octanol,

0955921-060600

dodecanol, stearyl alcohol, the various amyl alcohols, cyclohexanol and ethylene glycol monomethyl ether.

5 The substances which react with isocyanate must be selected in such a way that their average functionality does not exceed two if thermoplastically processable polyurethane elastomers are intended to be prepared. If higher functional compounds are used, the overall functionality must be lowered by means of monofunctional compounds.

10 The relative amounts of compounds (B1) and (B2) in (B) are preferably selected so that the ratio of the sum of isocyanate compounds in (A) to the sum of Zerewitinoff-active hydrogen atoms in (B) is 0.9 : 1 to 1.2 : 1, preferably 0.95 : 1 to 1.1 : 1.

15 Thermoplastic polyurethane elastomers according to the invention may contain up to a maximum of 20 wt.%, with respect to the total amount of TPU, of conventional auxiliary agents and additives as auxiliary agents and additives (C). Typical auxiliary agents and additives are catalysts, pigments, colorants, flame retardants, stabilisers against ageing and the effects of the weather, plasticisers, lubricants and mould release agents, substances which combat fungi and bacteria and fillers and
20 mixtures thereof.

Suitable catalysts according to the invention are conventional tertiary amines known from the prior art such as e.g. triethylamine, dimethylcyclohexylamine, N-methylmorpholine, N,N'-dimethylpiperazine, 2-(dimethylamino-ethoxy)-ethanol,
25 diazabicyclo[2.2.2]octane and the like and, in particular, also organic metal compounds such as titanates, iron compounds or tin compounds such as tin diacetate, tin dioctoate, tin dilaurate or the tin dialkyl salts of aliphatic carboxylic acids such as dibutyltin diacetate or dibutyltin dilaurate or the like. Preferred catalysts are organic metal compounds, in particular titanates, iron and tin
30 compounds. The total amount of catalysts in the TPUs according to the invention is

generally about 0 to 5 wt.%, preferably 0 to 2 wt.%, with respect to the total amount of TPU.

5 Examples of other additives are lubricants, such as fatty acid esters, their metal
soaps, fatty acid amides, fatty acid ester amides and silicone compounds, anti-
blocking agents, inhibitors, stabilisers to protect against hydrolysis, light, heat and
discoloration, flame retardants, colorants, pigments, inorganic and/or organic fillers
and reinforcing agents. Reinforcing agents are in particular fibrous reinforcing
10 agents such as e.g. inorganic fibres which are prepared in accordance with the prior
art and may also be provided with a coating of size. More detailed data on the
auxiliary agents and additives mentioned may be obtained from the specialist
literature, for example from the monograph by J.H. Saunders and K.C. Frisch "High
Polymers", vol. XVI, Polyurethane, part 1 and 2, Verlag Interscience Publishers
1962 and 1964, Taschenbuch für Kunststoff-Additive by R. Gächter and H. Müller
15 (Hanser Verlag Munich 1990) or DE-A 29 01 774.

Components (A) and (B) are mixed homogeneously in a reactor within a period of at
most 5 seconds. The thorough mixing preferably takes place with a small amount of
back-mixing. Homogeneous thorough mixing in the context of the invention means
20 that the concentration distribution of components (A) and (B) and of the reaction
product in the mixture has a relative standard deviation of less than 5 %. A small
amount of back-mixing in the context of this invention means that the residence time
in the reactor corresponds to that in a series of ≥ 10 ideal stirred tanks (stirred tank
cascade).

25 Before components (A) and (B) are introduced continuously into the reactor, they
must be heated, separately from each other, preferably in a heat exchanger, up to a
temperature between 60 and 220°C, preferably between 90 and 190°C. According to
the invention, it is essential that the temperatures of the two components (A) and (B)
30 differ by less than 20°C before being introduced into the reactor. The temperature

00955921 060600

difference between the component streams (A) and (B) is preferably $< 10^{\circ}\text{C}$, in particular $< 5^{\circ}\text{C}$.

5 The mixture obtained in this way is then converted into TPU in any type of reactor, preferably an extruder or a reaction tube.

10 According to the invention polyaddition is preferably performed in an insulated and preferably heatable static mixer. This has the advantage that it has no moveable parts and that homogeneous, thorough mixing with virtually no back-mixing can take place in the shortest possible time. Static mixers which can be used according to the invention are described in Chem.-Ing. Techn. 52, No. 4 on pages 285-291 and in "Mischen von Kunststoff und Kautschukprodukten", VDI-Verlag, Düsseldorf 1993.

15 Static mixtures in accordance with DE-C 23 28 795 are preferably used. The static mixers preferably have a length to diameter ratio of 8:1 to 16:1, in particular 10:1 to 14:1. The residence time in the static mixer is < 5 seconds, preferably < 2.5 seconds. The static mixers are preferably made from stainless steel, in particular from V4A.

20 In a further preferred embodiment, the process according to the invention is performed in a twin shaft extruder, whose shafts preferably rotate in the same direction. In this case the first part of the extruder can also be used to heat up the isocyanate component (A).

25 TPUs prepared by the process according to the invention may optionally be further processed, e.g. by annealing the polymer in the form of sheets or blocks, crushing or granulating in shredders or mills, degassing and granulating with melting. The polymer is preferably taken to a system for continuous degassing and extrudate production. This unit may be e.g. a multi-screw machine which if possible is provided with no kneading elements, or with only a few kneading elements.

30

0955921.060600

The present invention also provides the thermoplastic polyurethane elastomers obtained using the process according to the invention. It has to be regarded as surprising that the moulding compositions prepared according to the invention have a high degree of homogeneity and improved melting characteristics.

5

Thermoplastic polyurethane elastomers obtained according to the invention are preferably used to prepare films and readily melted coextruded products such as laminates, calandered products, hot melt adhesives and for powder-slush coextruded products.

009090 1265560

Examples

Example 1

5

1630 g/h of MDI and 2685 g/h of a mixture of polybutanediol adipate (average molecular weight $\overline{M}_n = 800$), which contained 200 ppm of a tin dioctoate, and butanediol in a ratio by weight of 6.9:1 were metered into a static mixer, separately from each other. The MDI and the polyol/butanediol mixture each had a temperature of $140 \pm 10^\circ\text{C}$. Premixing the components took place in a static mixer with all-round heating (model SMX, Sulzer AG) and with a diameter of 6 mm, a length of 6 cm and a rate of shear of 500 s^{-1} ; the reaction was performed in a reaction tube with mixing elements at the end.

10

15

Using this process, TPU could be produced for more than 90 minutes without a pressure increase being observed in the static mixer.

Example 2

20

This test was performed in the same way as in example 1 with the difference that the temperature of the reactant streams was $160 \pm 5^\circ\text{C}$. Even under these conditions, TPU could be produced for more than 90 minutes without a pressure increase being observed in the static mixer.

25

Example 3 (comparison)

30

The following temperature profile was preset in a reaction extrusion plant of the ZSK 83 type: housing 1-4: 120°C , housing 5-9: no temperature guidelines, housing 10-13: 120°C , head: 200°C . The same formulation as in example 1 was used, the rate of rotation was 300 rpm, the throughput 600 kg/h. MDI was metered into housing 1.

The temperature of the MDI at the entrance to housing 5 was about 90°C. The polyol/butanediol mixture with a temperature of 140°C was metered into housing 5.

The results of examples 1 and 2 and of comparison example 3 are given in Table 1.

5 The recrystallisation temperature was determined by DSC measurement with a calorimeter of the Perkin Elmer DSC 7 type. The product obtained in the comparison example had a peak maximum at a higher temperature during DSC measurement.

10 Whereas the melt flow index MFI for the TPUs prepared in the examples according to the invention increased by a factor of only 2 on increasing the temperature from 190°C to 200°C, this value increased by a factor of 5 in the comparison example. The low temperature dependence of the melt flow index MFI (ratio of MFI at 200°C to MFI at 190°C) and the higher MFI value of the TPUs prepared according to the invention indicate improved melting characteristics.

15

Table 1

	Example 1	Example 2	Example 3 (comparison)
Recrystallisation temperature T_c [°C]	85	87	102
Melt flow index MFI ** (190°C)[g/10 min]	27	25	4.7
Melt flow index MFI ** (200°C)[g/10 min]	55	52	20.3

** measured in accordance with ASTM D1238.

20

Example 4 (comparison)

The test was performed in the same way as example 1, but the temperature of the MDI at the entrance was 60°C and that of the polyol/butanediol mixture was 140°C.

25 After about 10-15 minutes, the pressure in the static mixer had already increased to >50 bar, so the experiment had to be terminated.

009090" 1265560

Using the industrially conventional high temperature difference of 80°C between the starting components, intense inhomogeneities are observed due to poor mixing. This leads to accretions in the static mixer due to cross-linking reactions or premature deposition of crystallites.

5

Example 5

1194 g/h of HDI and 3800 g/h of a mixture of polytetrahydrofuran (average molecular weight $\overline{M}_n = 1000$) and butanediol in the ratio by weight of 11.5:1 were metered separately into a static mixer. The temperatures of the HDI and polyol/butane diol mixture were each 90±10°C. A static mixer with all-round heating (model SMX, Sulzer AG) and with a diameter of 6 mm, a length of 6 cm and a rate of shear of 500 s⁻¹ was used to achieve mixing; the reaction was performed in an extruder at the end.

15

Example 6 (comparison)

The test was performed in the same way as in example 5, but HDI was introduced to the reactor at a temperature of 23°C and the polyol mixture was introduced at a temperature of 80°C.

20

The results of example 5 and comparison example 6 are given in Table 2. This shows that the TPU produced by the process according to the invention has improved melting characteristics. The low scatter among individual values of the melt flow index MFI within one measurement for the product prepared according to the invention may be taken to indicate a high degree of homogeneity.

25

00955921-060600

Table 2

	Example 5	Example 6 (comparison)
Recrystallisation temperature T_c [°C]	68	78
Melting point (°C)	180	190
Melt flow index MFI * (190°C)[g/10 min]	49.6±2	55 (scatter 32-60)

* measured in accordance with ASTM D1238.

5

Examples 7-10

TPU formulation:

1.0 moles polybutylene adipate, $\overline{M}_n=840$ g/mole

10 1.3 moles 1,4-butane diol

2.3 moles MDI

200 ppm tin dioctoate (with respect to polybutylene adipate)

0.2 wt.% Loxamide (with respect to the total amount of TPU)

15 The components were metered into an extruder of the ZSK 83 type, which operated at a speed of 300 rpm and had a throughput of 600 kg/h. The temperature profiles set via the housing temperatures of the extruder are given in Table 3. In examples 7-9, MDI was metered into the first housing and the polyol mixture consisting of polybutylene adipate and 1,4-butanediol was metered into the fifth housing in the

20 extruder. The temperature of the MDI in example 7 was about 60°C, in example 8 about 120°C, in example 9 about 130°C. In example 10, the MDI was heated to 130°C, the polyol mixture to 140°C, then both reactant streams were fed into the first housing. The catalyst was added to the polyol mixture each time, loxamide was admixed with the isocyanate.

0955921-060600

Table 3: Pre-set screw housing temperatures

Example	7	8	9	10
Housing 1	80°C	140°C	140°C	none
2	80°C	140°C	140°C	none
3	80°C	140°C	140°C	none
4	none	140°C	140°C	none
5	none	none	none	none
6	none	none	none	none
7	none	none	none	none
8	none	none	none	none
9	none	none	none	none
10	none	100°C	100°C	100°C
11	none	100°C	100°C	100°C
12	150°C	120°C	120°C	100°C
13	100°C	120°C	120°C	100°C
Head	200°C	200°C	200°C	200°C

5 Films were prepared from the products obtained using an extrusion blow moulding plant. The TPU granulate was melted in a single shaft extruder model 30/25D Plasticorder PL 2000-6 (Brabender Co.) (rate of addition 3 kg/h, temperatures 185-205°C) and extruded through a film blowing head to give a tubular film. The 100 % modulus of the product was determined in accordance with DIN 53504/NSI. The results are given in Table 4.

10

Table 4

Example	Temperature polyol mixture	Temperature MDI	Film properties: specks/structure	100% modulus
7*	150°C	50°C	many/very obvious	12
8*	140°C	120°C	some/obvious	11
9	140°C	130°C	very few/very little	11
10	140°C	130°C	none/none	11

* Comparison example, not according to the invention